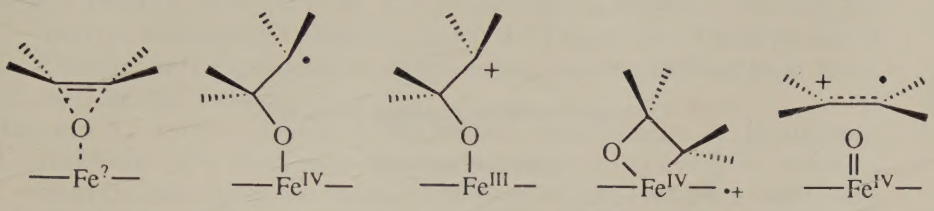
BIOORGANIC CHEMISTRY

An International Journal



I II III IV V

VOLUME 18 · 1990

EDITOR: Gordon A. Hamilton

EDITORIAL BOARD:

Robert H. Abeles
Duilio Arigoni
Jack E. Baldwin
Alan R. Battersby
Stephen J. Benkovic
Ronald Breslow
Thomas C. Bruice
David E. Cane
Peter B. Dervan
Debra Dunaway-Mariano
Fritz Eckstein
Perry A. Frey
Toshio Goto
John T. Groves
Jaak Järv
William P. Jencks
Yuichi Kanaoka
George L. Kenyon
Ronald H. Kluger
Gordon Lowe
Teruo Matsuura
Brian W. Metcalf
John F. Morrison
Koji Nakanishi
Janos Rétey
Irwin A. Rose
A. Ian Scott
Seiji Shinkai
JoAnne Stubbe
Joseph J. Villafranca
Christopher T. Walsh
George M. Whitesides
Richard V. Wolfenden
Burt Zerner

ACADEMIC PRESS, INC.
Harcourt Brace Jovanovich, Publishers

San Diego New York Boston
London Sydney Tokyo Toronto

Copyright © 1990 by Academic Press, Inc.

All rights reserved

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the copyright owner.

The appearance of the code at the bottom of the first page of an article in this journal indicates the copyright owner's consent that copies of the article may be made for personal or internal use, or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per copy fee through the Copyright Clearance Center, Inc. (27 Congress Street, Salem, Massachusetts, 01970) for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to other kinds of copying, such as copying for general distribution, for advertising or promotional purposes, for creating new collective works, or for resale. Copy fees for pre-1990 articles are as shown on the article title pages; if no fee code appears on the title page, the copy fee is the same as for current articles.

0045-2068/90 $3.00

MADE IN THE UNITED STATES OF AMERICA

This journal is printed on acid-free paper

CONTENTS OF VOLUME 18

NUMBER 1, MARCH 1990

MIKLÓS SIMONYI, GÁBOR MAKSAY, ILONA KOVÁCS, ZSUZSANNA TEGYEY, LÁSZLÓ PÁRKÁNYI, ALAJOS KÁLMÁN, AND LÁSZLÓ ÖTVÖS. Conformational Recognition by Central Benzodiazepine Receptors 1

TÓNU KESVATERA, AIN LANGEL, AND JAAK JÄRV. Salt Effects on Cholinesterase-Catalyzed Hydrolysis of Acetylcholine 13

TADASHI EGUCHI AND NOBUO IKEKAWA. Conformational Analysis of 1α,25-Dihydroxyvitamin D_3 by Nuclear Magnetic Resonance 19

ACHLA TREHAN, ROBERT S. H. LIU, YOSHINORI SCHICHIDA, YASUSHI IMAMOTO, KATSUKI NAKAMURA, AND TÔRU YOSHIZAWA. On Retention of Chromophore Configuration of Rhodopsin Isomers Derived from Three *dicis* Retinal Isomers 30

HUSSEIN Y. AFEEFY, DAVID J. BUCKTHAL, AND GORDON A. HAMILTON. Oxidation of a Putrescine–Glyoxylate Adduct Catalyzed by δ-Amino Acid Oxidase Gives the Product-Inhibitor 2-Carboxy-4,5,6,7-tetrahydro-1,3-diazepine 41

YUKITO MURAKAMI, YOSHIO HISAEDA, AND TERUHISA OHNO. Hydrophobic Vitamin B_{12}. 8. Carbon-Skeleton Rearrangement Reactions Catalyzed by Hydrophobic Vitamin B_{12} in Octopus Azaparacyclophane.... 49

JAMES LIGHT AND RONALD BRESLOW. The Hydrolysis of a Co(III) Chelated Amide Catalyzed by an Internal Phosphonic Acid Group 63

WILLIAM M. LOFFREDO AND MING-DAW TSAI. Phospholipids Chiral at Phosphorus: Synthesis and Configurational Assignment of Phosphorothioate Analogs of Phosphatidylserine 78

JOHN A. ZOLTEWICZ AND LINDA B. BLOOM. The Apparent pK_a of the Oxidation Product of Spermine or Spermidine: A pK_a Masked by a Ring-Chain Tautomeric Equilibrium 85

DENIS TRITSCH, OLIVIER MUNCH, AND JEAN-FRANÇOIS BIELLMANN. 4-Chloroacetylpyridine Adenine Dinucleotide, a Chromophoric Reagent for the Thiol Group—Study with Glutathione and with Aldehyde Dehydrogenase 91

NUMBER 2, JUNE 1990

HIDEO KISE. Difference in Catalytic Activities of Subtilisin Carlsberg and Subtilisin BPN′ and Immobilization–Activation for Ester Synthesis and Transesterification in Ethanol 107

RONALD L. HANSON, JANAK SINGH, THOMAS P. KISSICK, RAMESH N. PATEL, LASZLO J. SZARKA, AND RICHARD H. MUELLER. Synthesis of L-β-Hydroxyvaline from α-Keto-β-hydroxyisovalerate Using Leucine Dehydrogenase from *Bacillus* Species 116

TIANMEI OUYANG, DAVID R. WALT, AND SMITA S. PATEL. Enzyme-Catalyzed Synthesis of Citric Acid Using Acetyl-Coenzyme A Recycling in a Two-Phase System 131

Ronald Kluger and Marcel R. Trachsel. Differentiation of Diastereomeric Salts of Hydroxyethyl(thiamin) and Analysis of Stereochemical Requirements in Pyruvate Decarboxylase 136
Manickam Sugumaran, Hemalatha Dali, and Victor Semensi. Formation of a Stable Quinone Methide during Tyrosinase-Catalyzed Oxidation of α-Methyl Dopa Methyl Ester and Its Implication in Melanin Biosynthesis 144
Charles R. Johnson, Brian R. Boettcher, Richard E. Cherpeck, and Mark G. Dolson. Design and Synthesis of Potent Inhibitors of Glutamine Synthetase. 1. Cyclic Analogs of Phosphinothricin 154
Linda L. Szafraniec, William T. Beaudry, Leonard J. Szafraniec, and J. Richard Ward. Parallel Hydrolysis Paths for Nucleophilic Displacement on a Phosphonofluoridate 160
Ronald W. McClard and John F. Witte. Stable and Nonmetabolizable *C*-Glycosylphosphonyl Analogs of 5-Phosphorylribose 1-α-Diphosphate That Act as Inhibitors of Orotate Phosphoribosyltransferase 165
Theresa Rosario-Jansen, Henry Pownal, Ru-Tai Jiang, and Ming-Daw Tsai. Phospholipids Chiral at Phosphorus: Synthesis of Dioleoylthiophosphatidylcholine and Stereospecificity of Lecithin-Cholesterol Acyltransferase 179
Peter M. Gannett, Patrick Iversen, and Terence Lawson. The Mechanism of Inhibition of Cytochrome P450IIE1 by Dihydrocapsaicin 185
Patrice Talaga, Claude Benezra, and Jean-Luc Stampf. Stereochemistry of the Michael Addition of Lysine Derivatives to α-Methylene-γ-butyrolactones 199
Junghun Suh, Byung Keun Hwang, and Yung Hyo Koh. Bifunctional Catalysis by a Metal Ion and a Carboxylate Anion in Hydrolysis of an Alkyl Ester and an Alkyl Amide in Dimethyl Sulfoxide: A Carboxypeptidase A Model 207
John E. Baldwin, Naresh D. Ghatlia, and David W. Parker. Disparate Reactions of Thioesters of (Methylenecyclopropyl)acetic and β-(Cyclopropylidene)propionic Acids with Lithium Diisopropylamide and with General Acyl Dehydrogenase from Pig Kidney 221

Review

Mart Paberit. Kinetic Salting Effect as a Promising Tool in the Investigation of Enzyme Molecule Changes upon Reaction: Deacylation of Acyl-Chymotrypsins 228

Book Review

David C. Myles and George M. Whitesides. *Biotransformations in Preparative Organic Chemistry, The Use of Isolated Enzymes and Whole Cell Systems in Synthesis* by H. G. Davies, R. H. Green, D. R. Kelly, and Stanley M. Roberts 251

NUMBER 3, SEPTEMBER 1990

Kit-Sum Wong and Glenn Dryhurst. Tryptamine-4,5-dione: Properties and Reaction with Glutathione 253

PETER KOVACIC, MARK A. KASSEL, BENJAMIN A. FEINBERG, MICHAEL D. CORBETT, AND ROBERT A. MCCLELLAND. Reduction Potentials in Relation to Physiological Activities of Benzenoid and Heterocyclic Nitroso Compounds: Comparison with the Nitro Precursors 265
JUNGHUN SUH AND MINHAENG CHO. Kinetics of the Carboxypeptidase A-Catalyzed Hydrolysis of α-(Benzoylamino)cinnamoyl Derivatives of Various Amino Acids 276
YOSHIAKI KOBUKE AND JUN-YA YAMAMOTO. Cation Transport by Modified Dibenzo-18-Crown-6 through Lecithin Liposomal Membrane 283
MONIKA Z. WRONA AND GLENN DRYHURST. Electrochemical Oxidation of 5-Hydroxytryptamine in Aqueous Solution at Physiological pH 291
KAZUTAKA TANIZAWA, SINYA WATANABE, AND YUICHI KANAOKA. Fluorescence-Labeled *Streptomyces* Subtilisin Inhibitor: Analysis of the Interaction with Subtilisin and *Streptomyces griseus* Proteases 318
S. HALAZY, V. BERGES, A. EHRHARD, AND C. DANZIN. *Ortho-* and *para-*(Difluoromethyl)aryl-β-D-glucosides: A New Class of Enzyme-Activated Irreversible Inhibitors of β-Glucosidases 330

REVIEW
JUNGHUN SUH. Model Studies of Carboxypeptidase A 345

NUMBER 4, DECEMBER 1990

M. OROZCO, R. FRANCO, J. MALLOL, AND E. I. CANELA. Theoretical Study of the Acidic Strength of Amino Acid Side Chains 361
YUH-SHYONG YANG AND PERRY A. FREY. Solvent Effects on the Solvolysis of ADPβS 373
EILEEN K. JAFFE AND JAYANTHI S. RAJAGOPALAN. Nuclear Magnetic Resonance Studies of 5-Aminolevulinate Demonstrate Multiple Forms in Aqueous Solution 381
JOHN A. ZOLTEWICZ, LINDA B. BLOOM, AND WILLIAM R. KEM. Hydrolysis of Cholinergic Anabaseine and *N*-Methylanabaseine: Influence of Cosolvents on the Position of the Ring-Chain Equilibrium—Compensatory Changes 395
ELIZABETH A. MYATT AND IOANNIS SCARPA. Synthesis of Novel Polyethyleneimine Derivatives by Stepwise, Reversible Blocking of Primary and Secondary Amines 413
JAMES T. STIVERS AND MICHAEL W. WASHABAUGH. Synthesis and Purification of Racemic 2-(1-Hydroxyethyl)thiamine Revisited 425
DEXTER B. NORTHROP AND RONALD G. DUGGLEBY. Calculations of Intrinsic Isotope Effects and the Detection of Tunneling in Enzyme-Catalyzed Reactions 435

REVIEW
PETER W. WHITE. Mechanistic Studies and Selective Catalysis with Cytochrome P-450 Model Systems 440

BOOK REVIEW
SEIJI SHINKAI. *Calixarenes*. By C. David Gutsche 457

Erratum

Volume 18, Number 2 (1990): Linda L. Szafraniec, William T. Beaudry, Leonard J. Szafraniec, and J. Richard Ward, "Parallel Hydrolysis Paths for Nucleophilic Displacement on a Phosphonofluoridate," pp. 160–164 458

Author Index for Volume 18 459

Subject Index for Volume 18 461

Information for Authors

Bioorganic Chemistry publishes accounts of research that are at the interface of chemistry and biology. The guiding principle that the Editorial Board will follow in accepting manuscripts for publication is that the research either use the principles and techniques of organic and physical organic chemistry in attempting to solve some problem of relevance to biology, or describe chemical studies that are inspired by some biological observation. Within this context, manuscripts suitable for submission are ones that deal with such topics as: characterization of the chemistry involved in new enzymatic reactions and metabolic pathways; elucidation of enzyme mechanisms and structure; application of kinetic, isotopic, stereochemical, and spectral techniques to the study of enzymes and metabolic pathways; investigations of chemical model systems for enzymes, peptides, and other biological molecules; studies related to coenzyme structure and reactivity; development of catalyst systems that mimic enzymes and coenzymes; achievement of useful organic transformations by the application of enzymes; description of new chemistry that results from some finding in biology; development of mechanism-based and active site-directed inhibitors for enzymes, and characterization of the chemistry associated with their inhibition; investigation of the structure and mechanism of action of pheromones and other chemical communicants; determination of the molecular mechanisms for the action of hormones and of the molecular basis of pharmacology; elucidation of the principles involved in receptor site recognition; chemical modifications of nucleic acids and the application of such modifications to the manipulation of genetic material.

Manuscripts are accepted for review with the understanding that the same work has not been and will not be nor is presently submitted elsewhere, and that its submission for publication has been approved by all of the authors and by the institution where the work was carried out; further, that any person cited as a source of personal communications has approved such citation. Written authorization may be required at the Editor's discretion. Articles and any other material published in *Bioorganic Chemistry* represent the opinions of the author(s) and should not be construed to reflect the opinions of the Editor(s) and the Publisher.

Authors submitting a manuscript do so on the understanding that if it is accepted for publication, copyright in the article, including the right to reproduce the article in all forms and media, shall be assigned exclusively to the Publisher. The Publisher will not refuse any reasonable request by the author for permission to reproduce any of his or her contributions to the journal.

Although the journal will be devoted primarily to the publication of regular articles, Reviews and Preliminary Communications will also be published. In addition, Book Reviews and a Correspondence section will appear from time to time.

Regular articles must feature novel, previously unpublished material or represent full accounts of findings published earlier in preliminary form.

An acceptable *Review* may embrace the results of various workers in a given area or may feature recent developments from the author's own laboratory. A review that is distinguished by a novel interpretation or representation of earlier findings is especially suitable. The Editor welcomes inquiries concerning the suitability of a particular topic for a review article.

Preliminary Communications will receive accelerated publication and should describe particularly novel and significant new findings. They should be accompanied by a brief abstract and should not exceed 5 printed pages in length (approximately 3000 words), including references, tables, and figures.

Letters to the Editor offering interpretations of data that are different from those published by other authors will be entertained and, along with the original authors' rebuttal, will be considered for inclusion in the *Correspondence* section. It is hoped that this section will offer a forum where points of contention concerning various topics of interest to the field of bioorganic chemistry can be discussed in print. From time to time this section will also include announcements and summaries of meetings that are of interest to bioorganic chemists.

Address all submitted manuscripts and correspondence to:

Dr. Gordon A. Hamilton
Editor, *Bioorganic Chemistry*
Department of Chemistry
152 Davey Laboratory
Pennsylvania State University
University Park, Pennsylvania 16802

Manuscripts should be written in a clear and accurate fashion with careful attention to detail. Submit manuscripts (in English) in quadruplicate (one original and three copies), with copies of graphs, drawings, organic structural formulas, etc., suitable for direct reproduction. All material (including tables, legends, reference lists, and footnotes) should be typed double spaced on one side of $8\frac{1}{2} \times 11$-in. white bond paper with 1-in. margins on all sides. Each page of the manuscript should be numbered. Page 1 should contain the article title, author's name (without degrees), affiliation, a short running title (not exceeding 45 letters and spaces), and an address to which proof should be mailed. Page 2 should contain a short abstract. Acknowledgments may be included as a separate section.

All nomenclature should be simple, unambiguous, and in conformity with the conventions developed by Chemical Abstracts and the International Union of Pure and Applied Chemistry. For further information regarding nomenclature, authors are advised to consult the Instructions to Authors of the *Archives of Biochemistry and Biophysics* (1988) **260,** xx–xxvi. *Reprints are available from the Publisher.*

In the Methods section, authors should draw attention to any particular chemical or biological hazards that may be involved in carrying out the experiments described. Any relevant safety precautions should be described; if an accepted code of practice has been followed, a reference to the relevant standards should be given.

Abbreviations should be in accordance with the International System (SI) as adopted by the 11th General Conference on Weights and Measures. Common abbreviations are: meter, m; centimeter, cm; millimeter, mm; micrometer, μm; nanometer, nm; kilogram, kg; gram, g; milligram, mg; microgram, μg; nanogram, ng; milliliter, ml; microliter, μl; molar, M; millimolar, mM; micromolar, μM; normal, N, millicurie, mCi; microcurie, μCi; counts per minute or second, cpm or cps; disintegrations per minute or second, dpm or dps; centigrade, °C; seconds, s; minutes, min; hours, h; standard deviation, SD; standard error, SE; percent, %; melting point, mp; boiling point, bp; calorie, cal; kilocalorie, kcal; nuclear magnetic resonance, NMR; infrared, ir; ultraviolet, uv; number, No.; Ångstrom units, Å; cycles per second, Hz; parts per million, ppm; Equation, Eq.

Tables must appear on a separate sheet with a descriptive title typed double spaced above the table. Tables must be numbered consecutively with Arabic numerals in order in the text.

Figures and graphs are to be numbered consecutively in Arabic numerals and cited in order in the text; legends should be typed double spaced on a separate sheet. Graphs should be plotted with black India ink on white paper no larger than $8\frac{1}{2} \times 11$ in., with coordinates properly labeled; grid lines that are shown in the engraving should be inked in black. Original drawings no larger than $8\frac{1}{2} \times 11$ in. (21×27.5 cm) are preferred. The following standard symbols should be used in the legends to the figures because they are readily available to the printers:

▲ □ ■ ○ ● ⊙ × ◈ ◆.

Photographs should be kept to a minimum and should be glossy prints with strong contrasts; the magnification should be indicated by a scale where possible. Illustrations in color can be accepted only if the authors defray the cost.

Structural formulas and chemical equations should be typed or drawn with care, and arranged to fill space economically. Since chemical structures will be reproduced directly from manuscript copy, authors are asked to prepare such material using appropriate templates and to check it carefully before manuscript submission.

Footnotes should be designated in text by superscript numbers and listed on a separate sheet, starting with the title; in tables they should be noted by superscript letters and placed at the bottom of the page containing the table.

References to the literature should be cited in the text by underlined Arabic numerals in parentheses. They must appear on a separate sheet, listed in numerical order, i.e., in accordance with order of citation in the text. Styling of references should conform to the following format (authors should refer to *Chemical Abstracts Service Source Index,* 1985, for styling of journal titles):

1. Hamilton, G. A., and Buckthal, D. J. (1982) *Bioorg. Chem.* **11,** 350–370.
2. Jardetsky, O., and Roberts, G. C. K. (1981) NMR in Molecular Biology, pp. 417–447, Academic Press, New York.
3. Oppenheimer, N. J. (1982) *in* The Pyridine Nucleotide Coenzymes (Everse, J., Anderson, B., and You, K., Eds.), pp. 51–89, Academic Press, New York.

Proofs will be sent to the corresponding author. Authors will be charged for excessive alterations.

Fifty reprints of each article will be supplied free of charge. Additional reprints may be purchased; an order form will accompany proofs.